REMARKS

Reconsideration and allowance are respectfully requested.

Claims 1-18 are pending. The claim amendments are supported by our disclosure as originally filed. No new matter is added by their entry. Support for amendment of claims 1 and 9 is found at page 4, lines 18-20, "In a preferred embodiment, the aqueous composition used in the method according to the present invention is . . . an aqueous dispersion such as an emulsion or suspension."

Entry of the claims amendments and the evidence of non-obviousness submitted herewith (i.e., US 5,714,135) is requested to rebut the obviousness rejection. They could not be earlier presented because the Suloff thesis was not cited as part of the Section 103(a) rejection until the final Office Action. Their entry will reduce the issues on appeal.

35 U.S.C. 103 – Nonobviousness

A claimed invention is unpatentable if the differences between it and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art. *In re Kahn*, 78 USPQ2d 1329, 1334 (Fed. Cir. 2006) citing *Graham v. John Deere*, 148 USPQ 459 (1966). The *Graham* analysis needs to be made explicitly. *KSR v. Teleflex*, 82 USPQ2d 1385, 1396 (2007). It requires findings of fact and a rational basis for combining the prior art disclosures to produce the claimed invention. See id. ("Often, it will be necessary for a court to look to interrelated teachings of multiple patents . . . and the background knowledge possessed by a person having ordinary skill in the art, all in order to determine whether there was an apparent reason to combine the known elements in the fashion claimed by the patent at issue"). The use of hindsight reasoning is impermissible. See id. at 1397 ("A factfinder should be aware, of course, of the distortion caused by hindsight bias and must be cautious of arguments reliant upon *ex post* reasoning"). Thus, a *prima facie* case of obviousness under Section 103(a) requires "some rationale, articulation, or reasoned basis to explain why the conclusion of obviousness is correct." *Kahn*, 78 USPQ2d at 1335; see *KSR*, 82 USPQ2d at 1396. An inquiry should be made as to

"whether the improvement is more than the predictable use of prior art elements according to their established functions." Id. at 1396. But a claim which is directed to a combination of prior art elements "is not proved obvious merely by demonstrating that each of its elements was, independently, known in the prior art." Id. at 1396. Finally, a determination of prima facie obviousness requires a reasonable expectation of success. See *In re Rinehart*, 189 USPQ 143, 148 (C.C.P.A. 1976).

Claims 1-18 were rejected under Section 103(a) as allegedly unpatentable over the Suloff thesis, Isom et al. (EP 1,174,039) and Ang (EP 1,068,809) in view of Noordam et al. (US 5,552,151), De Haan et al. (EP 867,124), and Schuppiser et al. (US 5,446,014). Applicants traverse because their claimed invention is directed to solving the problem of nozzle clogging when shredded cheese is sprayed with an aqueous composition containing natamycin by including a thickening agent. The prior art teaches away from the invention and does not establish a reasonable expectation of success.

In accordance with Applicants' invention, the presence of a thickening agent in an aqueous composition containing natamycin prevents nozzle clogging, which otherwise occurs when spraying shredded cheese with the aqueous composition. There is no evidence of record that the presence of a thickening agent in the aqueous composition containing natamycin would have had this effect. Instead, Suloff solved the problem by using chemical derivatives of natamycin which do not clog the nozzle. The natamycin derivatives are soluble in an aqueous composition whereas natamycin is dispersed in the aqueous composition according to Applicants' claims as presently amended. Suloff teaches away from using a dispersion of natamycin.

Isom added a nutritional supplement comprising calcium sulfate dehydrate to the shredded cheese. Use of this supplement reduced the amount of anti-caking agents commonly present in shredded cheese at high levels (see column 2, lines 36-41). Isom disclosed that natamycin can also be added to shredded cheese. The use of thickening agents, however, to prevent nozzle clogging during spraying of an aqueous composition containing natamycin is neither taught nor rendered obvious by Isom. No thickening agent was used in the cited document.

Ang relates to increasing the bioavailability of natamycin (see page 2, paragraph [0008]). It solved the clogging problem by reducing the average particle size of natamycin to below 10 microns (see page 3, paragraphs [0017] and [0018]). It disclosed that the natamycin can be added to the shredded cheese by dry mixing instead of spraying. The use of a thickening agent, however, to prevent nozzle clogging during spraying of an aqueous composition containing natamycin is neither taught nor rendered obvious by Ang. Instead, the cited document's only solutions to the clogging problem were reducing the particle size of natamycin and avoiding spraying all together. Therefore, Ang teaches away from being combined with the other cited documents because it would be simpler to add natamycin to shredded cheese by dry mixing at the same time the anti-caking agent is added, in contrast to spraying the natamycin separate from mixing with the anti-caking agent (see Applicants' claim 1). One of ordinary skill in the art would not have cited Ang to render obvious the claimed invention, which requires the separate addition of anti-caking agent and natamycin to the shredded cheese as in claim 1.

Noordam combined natamycin and a thickening agent (e.g., xanthan) to stabilize a concentrated suspension. Using the thickening agent, however, to prevent nozzle clogging during the spraying of an aqueous composition containing natamycin is not taught or rendered obvious by the cited document. De Haan is directed to an aqueous composition containing natamycin and xanthan gum. But prevention of nozzle clogging when spraying an aqueous composition containing natamycin is not addressed.

Schuppiser relates to the problem of nozzle clogging of aqueous formulations of quaternary ammonium hydroxides and xanthan gum due to the formation of insoluble fibers (see column 1, lines 53-61). But quaternary ammonium compounds are structurally different from polyene antifungal antibiotics like natamycin. They also have different chemical properties. There is also no evidence of record establishing that quaternary ammonium hydroxides could have been replaced by natamycin with a reasonable expectation of success. On the contrary, one of ordinary skill in the art would have had serious doubts as to whether Schuppiser's methods would be applicable to an aqueous composition containing natamycin because of structural and chemical differences therebetween. It is submitted that any argumentation to the contrary is based on hindsight.

To summarize, the primary documents relied upon in this rejection do not teach or render obvious Applicants' solution to preventing nozzle clogging when natamycin is sprayed on shredded cheese. Suloff taught that the chemical structure of natamycin should be changed. Ang taught that the particle size of natamycin should be reduced or it should be mixed with the shredded cheese instead of sprayed. Isom, Noordam, and de Haan have nothing to say about solving the problem of nozzle clogging. Schuppiser does not render Applicants' invention obvious because natamycin would not have replaced quaternary ammonium hydroxides with a reasonable expectation of success.

Therefore, the documents cited in this rejection, alone or in combination, do not render obvious including a thickening agent in an aqueous composition containing natamycin to prevent nozzle clogging. On the contrary, the cited documents suggest that the problem of nozzle clogging can be solved by changing natamycin's chemical structure or reducing its particle size. Further, the combined documents do not render obvious separately adding to shredded cheese (i) anti-caking agent by mixing and (ii) natamycin by spraying (cf. claim 1). Combining the cited documents creates irreconcilable conflicts between their teachings instead of establishing a *prima facie* case of obviousness.

Further, separating the mixing of an anti-caking agent with shredded cheese from the spraying of shredded cheese with an aqueous composition containing natamycin is not addressed, nor does it appear to have been contemplated. In particular, Ang taught away from this limitation of claim 1 by the suggestion that both anti-caking agent and natamycin could be mixed with the shredded cheese at the same time.

Suloff should also not be combined with the other documents in this rejection because it taught away from adding a thickening agent to an aqueous composition containing natamycin. Colloidal dispersion complexes were discussed negatively on pages 6-7. The aqueous insolubility of polyene macrolide antibiotics was caused by their intramolecular aggregation. Natamycin is a polyene macrolide antibiotic. Even use of a detergent did not solubilize the antibiotic in an aqueous composition. Suloff's natamycin derivatives, however, are soluble in water. The natamycin derivatives do not form colloidal dispersion complexes. Therefore, Suloff teaches away from being combined with the other cited documents if the combination would result in a dispersion of nata-

mycin (e.g., suspension or emulsion) in the aqueous composition. One of ordinary skill in the art would not have cited Suloff to render obvious the claimed invention, which requires a dispersion as presently claimed.

Moreover, since the composition will be sprayed, one of ordinary skill in the art would not have found it obvious to add a thickening agent to an aqueous composition that is sprayed. It was known in the art that inclusion of a thickening agent increases the risk that the composition forms a gel and exacerbates the problem of nozzle clogging. In evidence thereof, a copy of US 5,714,135 is submitted herewith. The '135 patent states,

> "Clogging of nozzle orifices is a perennial problem. Most often clogging is encountered with relatively viscous formulations, frequently the result of thickeners settling within the exit orifices"

(column 1, lines 17-22). Therefore, one of ordinary skill in the art would not have added a thickening agent to an aqueous composition containing natamycin.

For the reasons provided above, the combination of cited documents does not render obvious Applicants' claimed invention. See independent claims 1 and 9. Moreover, claims depending from the independent claims are also rendered obvious since the limitations of claim 1 or 9 are incorporated in the dependent claims. M.P.E.P. § 2143.03 citing *In re Fine*, 5 USPQ2d 1596 (Fed. Cir. 1988).

Withdrawal of the Section 103 rejection is requested because the claims would not have been obvious to one of ordinarily skill in the art when this invention was made.

Having fully responded to the pending Office Action, Applicants submit that the claims are in condition for allowance and earnestly solicit an early Notice to that effect. The Examiner is invited to contact the undersigned if any further information is required.

Respectfully submitted,

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United States Patent [19]

Lee et al.

[11] Patent Number: 5,714,135

[45] Date of Patent: Feb. 3, 1998

[54] HAIR TREATMENT COMPOSTION

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[51] Int. Cl.[6] A61K 7/06; A61K 7/11

[52] U.S. Cl. 424/70.11; 424/70.31; 424/DIG. 2

[58] Field of Search 424/70.11, 70.31, 424/DIG. 2

[56] References Cited

U.S. PATENT DOCUMENTS

4,315,910	2/1982	Nowak, Jr. et al. .	
4,983,377	1/1991	Murphy et al. .	
4,983,383	1/1991	Maksimoski et al. .	
5,034,220	7/1991	Helloff et al. .	
5,034,486	7/1991	Tzai et al. .	
5,066,481	11/1991	Helloff et al. .	
5,266,308	11/1993	Lee et al. .	

FOREIGN PATENT DOCUMENTS

0 584 877	3/1994	European Pat. Off. .
0 617 954	10/1994	European Pat. Off. .
0 686 386	12/1995	European Pat. Off. .
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"Stabileze® Thickeners and Stabilizers", ISP Product Brochure 1995.

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[57] ABSTRACT

A hair treatment composition for use with spray dispensers is provided which includes a crosslinked C_1–C_{10} alkyl vinyl ether/maleic anhydride copolymer, a nonionic, surfactant and a film-forming resin. Preferably the compositions are transparent gels. They exhibit reduced clogging of spray nozzle pumps and provide excellent sensory properties.

6 Claims, No Drawings

HAIR TREATMENT COMPOSTION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a hair styling composition. especially a sprayable gel dispensed through a pump mechanism.

2. The Related Art

Hairspays are products containing a film-forming resin which when applied to hair helps to hold the hair in place. Resins can be sprayed onto the hair utilizing different types of dispensers. Two of the most popular are the mechanical air driven pump container and the aerosol canister, the latter employing a volatile propellant to discharge product. Both types of dispensers include a spray nozzle through which product is sprayed.

Clogging of nozzle orifices is a perennial problem. Most often clogging is encountered with relatively viscous formulations, frequently the result of thickeners settling within the exit orifices. Carbomers which are the thickeners of choice in commercial products have especially been linked to plugging of orifices.

U.S. Pat. No. 4,983,377 (Murphy et al.) describes the use of silicone gums as highly effective conditioning and style retention aids. However, materials of this type may have deficiencies with respect to clogging. Improved materials are therefore necessary which can combine thickening, conditioning and style retention while still allowing for good sprayability.

Accordingly, it is an object of the present invention to provide a hair treatment composition suitable for dispensing through a pump without causing clogging of nozzles.

Another object of the present invention is to provide a hair treatment composition suitable for dispensing through a pump that not only provides excellent spray characteristics but also delivers excellent sensory properties.

Still another object of the present invention is to provide a hair treatment composition in the form of a clear gel with the properties of good sprayability, good styling and minimal tackiness.

These and other objects of the present invention will become more apparent from the detailed description which follows.

SUMMARY OF THE INVENTION

A hair treatment composition is provided including:

(i) from 0.01 to 10% by weight of a crosslinked C_1–C_{10} alkyl vinyl ether/maleic anhydride copolymer;

(ii) from 0.1 to 20% by weight of a film-forming resin; and

(iii) from 0.01 to 10% by weight of a nonionic surfactant.

DETAILED DESCRIPTION OF THE INVENTION

Now it has been discovered that a crosslinked alkyl vinyl ether/maleic anhydride copolymer in conjunction with a nonionic surfactant can deliver a film-forming polymer in aqueous solution as a uniform continuous spray. Clogging of pump nozzle orifices is no longer a significant problem. Moreover, these compositions deliver excellent sensory properties including conditioning, styling and luster.

A first essential element of the present invention is a crosslinked C_1–C_{10} alkyl vinyl ether/maleic anhydride copolymer to serve as a thickening agent for the hair

treatment composition. Most preferred is methyl vinyl ether/maleic anhydride copolymer crosslinked with 1,9-decadiene, commercially available as Stabileze QM® from ISP Corporation, Wayne, N.J. Particle size of the copolymer in powder form is preferably less than 100 micron. Amounts of the copolymer may range from 0.01 to 10%, preferably from 0.1 to 2%, optimally from 0.15 to 0.5% by weight.

The maleic anhydride segment of copolymers of this invention are preferably at least partially neutralized with base so that the copolymer becomes anionic. Suitable bases include sodium hydroxide, potassium hydroxide, ammonium hydroxide, triethanolamine, aminomethyl propanol, aminomethyl propanediol, tromethamine and tetrahydroxypropylethylenediamine. Amounts of the base relative to copolymer may range from 0.5:1 to 3:1.

A second essential element of the present invention is a nonionic surfactant. Generally this will be an ethoxylated or propoxylated adduct of a hydrophobe such as a C_8–C_{22} fatty alcohol, C_8–C_{22} fatty acid, C_8–C_{22} fatty amine, C_8–C_{15} alkylphenol, C_{12}–C_{18} fatty acid sorbitan esters and C_{12}–C_{18} fatty acid mono- and diglycerides. The amount of ethylene oxide or propylene oxide per mole of hydrophobe may range from 1 to 50 moles. More particularly the range of alkoxylation may range from 12 to 40 moles ethylene oxide or propylene oxide, most preferably from 20 to 30 moles. Particularly preferred are the ethoxylated nonionics, especially ethoxylated C_8–C_{22} fatty alcohols. Quite effective are the C_{18}–C_{22} fatty alcohols ethoxylated with from 20 to 30 moles ethylene oxide. Illustrative is polyethylene glycol 20-stearyl ether, known in CTFA nomenclature as Steareth-20, available commercially as Arosurf 66E-20.

A third essential element of the present invention is a water soluble film-forming resin. The resin may either be anionic, nonionic, amphoteric or cationic. Specific resins include polyvinylpyrrolidone (PVP), copolymers of (PVP) and methylmethacrylate, copolymers of PVP and vinyl acetate (VA), polyvinyl alcohol (PVA), copolymers of PVA and crotonic acid, copolymers of PVA and maleic anhydride, hydroxypropyl cellulose, hydroxypropyl guar gum, sodium polystyrene sulfonate, PVP/ethylmethacrylate/methacrylic acid terpolymer, vinyl acetate/crotonic acid/vinyl neodecanoate copolymer, octylacrylamide/acrylates copolymer, monoethyl ester of poly(methyl vinyl ether/maleic acid), and octylacrylamide/acrylate/butylaminoethyl methacrylate copolymers. Mixtures of resins may also be used. PVP and PVP copolymers with other monomers are preferred. The most preferred resins for use in the present hairsprays are copolymers of polyvinyl pyrrolidone and vinyl acetate, particularly a 70/30 ratio.

Amounts of the film-forming resin may range from 0.1 to 20%, preferably from 1 to 10%, optimally from 2 to 5% by weight.

Water will be present in compositions of the present invention. Amounts may range from 50 to 99%, preferably from 85 to 96% by weight.

Compositions of the present invention may be formulated as transparent or opaque emulsions, lotions, creams, pastes, mousses or gels. A particularly preferred form is that of a transparent gel having a viscosity sufficiently mobile for dispensing through a spray nozzle of a pump.

Compositions of the present invention will exhibit a pH ranging from 4.0 to 6.0, most preferably from 4.5 to 5.3.

Compositions of this invention advantageously can include hair conditioning agents. These agents may be selected from silicone compounds, quaternary ammonium polymers, phytantriol and mixtures thereof. Phytantriol is

particularly useful because it not only conditions but adds stylability to hair-care compositions. Phytantriol as known by its CTFA name is a hydrophobic branched triol chemically identified as 3,7,11,15-tetramethyl-1,2,3-hexadecanetriol. Commercially it is available from Hoffmann-La Roche, Inc., Nutley, N.J. For purposes of the present invention, the amount of phytantriol will range from 0.0001 to 1%, preferably from 0.001 to 0.5%, optimally from 0.005 to 0.2% by weight.

Silicone compounds may be chosen from volatile and non-volatile silicone fluids. Volatile silicone fluids are preferably oils chosen from cyclic or linear polydimethyl siloxanes containing from 3 to 9, preferably from 4 to 5 silicon atoms.

Cyclomethicone is the most preferred cyclic volatile silicone. Linear volatile silicone oils generally have viscosities less than about 5 centistokes at 25° C. while cyclic fluids typically have viscosities of less than about 10 centistokes.

Nonvolatile silicone oils useful for the present invention include polyalkyl siloxanes, polyalkylaryl siloxanes and polyether siloxane copolymers. Non-volatile polyalkyl siloxanes useful herein include, for example, polydimethyl siloxanes with viscosities of from 5 to 100,000 centistokes at 25° C. Among the preferred non-volatile silicones are the polydimethyl siloxanes having viscosities from 10 to 400 centistokes at 25° C. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

The non-volatile polyalkylaryl siloxane fluids that may be used include, for example, polymethylphenylsiloxanes having viscosities of about 15 to 30,000 centistokes at 25° C. Extremely high molecular weight silicones known as silicone gums ordinarily will not be employed in compositions of this invention.

Among the quaternary ammonium polymeric conditioners, the most useful are the cationic guar gums. The CTFA name for a preferred guar gum is guar hydroxypropyltrimonium chloride. This material is available from Rhone-Poulenc under the trademark Jaguar®. Illustrative is Jaguar® C13S, having a low degree of substitution of cationic groups and a high viscosity. Other suitable varieties are Jaguar® C15, having a moderate degree of substitution and a low viscosity; Jaguar® C17 having a high degree of substitution and a high viscosity; and Jaguar® C16 which is a hydroxypropylated cationic guar derivative containing a low level of substituent groups as well as cationic quaternary ammonium groups. Also suitable is Jaguar® 162 which is a high transparency, medium viscosity guar having a low degree of substitution. Especially preferred is Jaguar® C13S.

Also includable are minor amounts of other ingredients commonly found in hair care compositions, such as preservatives, keratin amino acids, UV inhibitors, fragrances, coloring agents, buffering agents, polyols and other moisturizing agents, herb extracts, mink oil or honey.

The following examples will more fully illustrate the embodiments of the present invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

EXAMPLES 1–5

The following transparent gel compositions are representative of the present invention.

	EXAMPLE (WEIGHT %)				
INGREDIENTS	1	2	3	4	5
PVP/VA (70/30 ratio; 50% solids)	8.0	---	12.0	6.0	---
PVP (50% solids)	---	8.0	---	---	6.0
Arosurf ® 66E-20 (Polyethylene glycol 20-stearyl ether)	0.8	0.8	1.2	0.6	0.6
Stabilcze ® QM (Methyivinyl ether/ Maleic Anhydride Copolymer)	0.24	0.24	0.1	0.50	0.50
Fragrance	0.1	0.1	0.1	0.1	0.1
Caustic Soda	0.07	0.07	0.07	0.07	0.07
Glydant Plus ® (DMDM Hydantoin)	0.05	0.05	0.05	0.05	0.05
Crotein ® HKP (Hair Keratin Amino Acids)	0.01	0.01	0.01	0.01	0.01
Uvinul ® MS-40 (UV Inhibitor)	0.002	0.002	0.002	0.002	0.002
Phytantriol (3,7,11,15-tetramethyl-1,2,3-hexadecanetriol)	0.001	0.001	0.001	0.001	0.001
Water	balance	balance	balance	balance	balance

EXAMPLE 6

Various surfactants were evaluated for their effect upon the gel structure of hair treatment compositions according to the present invention. A gel base essentially identical to Example 1 but absent surfactant was employed for evaluation purposes. This base contained 0.24% Stabilcze® QM and 7.5% Luviskol® VA 73W (PVP/VA in 70/30 ratio).

The gel base was divided into six groups. Each was formulated with 0.8% surfactant, except for one group which was employed as a control. Among the surfactants were two anionic (ammonium lauryl sulfate and sodium lauroyl sarcosinate), one cationic (cetrimonium chloride), one amphoteric (cocamidopropyl betaine), and one nonionic (steareth-20) surfactant. Results are reported in the Table below.

SURFACTANTS	GEL STRUCTURE	SPRAY CHARACTERISTICS	SURFACE TENSION
Ammonium Lauryl Sulfate	broke down (14 cps)	good	35.2 dynes/cm
Sodium Lauroyl Sarcosinate	broke down (46 cps)	good	31.1 dynes/cm
Cocamido Propyl Betaine	broke down (26 cps)	good	31.5 dynes/cm
Steareth-20	very good (14,000 cps)	very good	42.9 dynes/cm
Cetrimonium Chloride	broke down	poor	---
No Surfactant	very good (14,000 cps)	good	62.2 dynes/cm

Evident from the Table is that the gel structure achieved by the combination of Stabilcze® and Luviskol® VA 73W broke down in the presence of both anionic surfactants, the cationic and amphoteric surfactants. Only the nonionic surfactant retained the gel structure; it was also the only formulation that had very good spray characteristics.

EXAMPLE 7

Nozzle orifice clogging is a constant problem in pump hairstyling products, especially with relatively thick viscous

formulations. Film-forming resins and thickeners tend to settle within the exit orifices. Carbomers, the thickeners most often employed in commercial hair gel spray products, have been linked to the clogging phenomena.

The following experiments were conducted to evaluate the anti-clogging effects of compositions according to the present invention. The gel product of Example 1 (with Arosurf® 66E-20) was compared to DEP® Spray Gel, a leading commercial product. Example 1 and the DEP® Spray Gel had viscosities of 11,000 cps and 8,000 to 10,000 cps, respectively. Each was divided into six separate samples. These were sprayed in 10–12 strokes daily except for weekends over a four week period.

During this time, none of the Example 1 product showed any sign of orifice clogging. By contrast, the DEP® Spray Gel had 4 partial or severe blockages. Further, it was observed that the Example 1 product was smoother, softer and had better defined spray characteristics than that of the commercial product. Since both of the products utilize the same pump mechanism, the main difference between the two is believed to be in the rheology of the gel products.

Although this invention has been described with reference to specific examples, it will be apparent to one skilled in the art that various modifications will be suggested, all of which are within the spirit and purview of this invention.

What is claimed is:

1. A hair treatment product comprising:

(a) a pump dispenser including a spray nozzle through which a hair treatment composition is sprayed; and

(b) a hair treatment composition contained within the dispenser comprising:

(i) from 0.01 to 10% by weight of a crosslinked C_1–C_{10} alkyl vinyl ether/maleic anhydride copolymer;

(ii) from 0.1 to 20% by weight of a film-forming resin; and

(iii) from 0.01 to 10% by weight of a nonionic surfactant which is a C_8–C_{22} fatty alcohol ethoxylated with from 12 to 40 moles ethylene oxide.

2. The product according to claim 1 wherein the nonionic surfactant is polyethylene glycol 20-stearyl ether.

3. The product according to claim 1 wherein the copolymer is methylvinyl ether/maleic anhydride copolymer crosslinked with 1,9-decadiene.

4. The product according to claim 1 wherein the film-forming resin is selected from the group consisting of polyvinylpyrrolidone, copolymers of polyvinylpyrrolidone and methylmethacrylate, copolymers of polyvinylpyrrolidone and vinyl acetate, polyvinyl alcohol, copolymers of polyvinyl alcohol and crotonic acid, copolymers of polyvinyl alcohol and maleic anhydride, hydroxypropyl cellulose, hydroxypropyl guar gum, sodium polystyrene sulfonate, polyvinyl pyrrolidone/ethylmethacrylate/methacrylic acid terpolymer, vinyl acetate/crotonic acid/vinyl neodecanoate copolymer, octylacrylamide/acrylates copolymer and octylacrylamide/acrylate/butylaminoethyl methacrylate copolymers and mixtures thereof.

5. The product according to claim 1 wherein the water soluble film-forming resin is polyvinylpyrrolidone/vinyl acetate.

6. The product according to claim 1 further comprising from 0.0001 to 1% phytantriol.

* * * * *